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Radiationless Loss Mechanisms and Intermolecular Interactions

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FINAL REPORT

The research supported by the present contract has been very fruitful. In addition to educating three graduate students and two postdoctoral fellows, it has resulted in ten extremely valuable publications.

Due to the educational process, a large part of the work has just been written and sent for publication during the past year. For this reason, we have not sent technical reports. We are presently preparing the technical reports, and will be distributing them soon.

The research work carried out in the three-year period covered by the contract can be summarized under the following titles:

- I. The phosphorescence emission in crystals.
- II. The effect of shallow traps on the triplet-triplet annihilation process at very low temperature.
- III. The radiative and nonradiative properties of the individual multiplets of the lowest triplet state.
- IV. Review of the field of triplet state spectroscopy.

A summary of the work is presented below. At the end of each summary section, reference is made by number (see end of report) to publication(s) describing the details of the work.

I. The Phosphorescence of Crystalline Pyrazine:

The high-resolution phosphorescence spectrum of pyrazine crystals has been recorded and analyzed. The fact that the crystal structure of pyrazine crystal is known and that the ground-state molecular and lattice vibrations are assigned, made it possible to accurately analyze and assign the observed spectrum. The comparison of the observed spectrum obtained from pyrazine crystals with that obtained from pyrazine in cyclohexane

matrix at 4.2°K leaves no doubt that the observed emission from the crystals results from the ${}^3B_{3u} \rightarrow {}^1A_g$, $\pi^* \rightarrow n$ transition of the pyrazine molecule. The 0,0,0 band in emission is found to be 102 cm^{-1} lower in energy than the 0,0,0 band in absorption. This might suggest that the emission centers have slightly different environment and thus lower energy than those absorbing the radiation. This difference in environment also leads to the trapping of triplet excitons by pyrazine molecules located at physical defects. The different types of trapping mechanisms are briefly discussed in the light of the observed spectrum. There is a strong coupling between the electronic motion and the lattice modes of b_{3g} symmetry (the most prominent ones have frequencies of 57 and 82 cm^{-1}). The intensity of the emission of the phononic and phonon-vibronic bands is greater than that of the vibronic bands. This observation suggests that either the lattice parameters are different in the excited triplet state from those in the ground state or else there is a lattice-induced emission resulting from the coupling of the different molecular electronic states of pyrazine with lattice vibrations. These two mechanisms of phonon enhancement of the emission are discussed in terms of the site symmetry of the emitting pyrazine molecules at the trapping sites. Spectral evidence is given showing the coupling between the intramolecular C-H in-plane bending vibrations and the lattice modes. The b_{3g} lattice modes are found to have lower frequencies when coupled to the C-H in-plane bending vibration than when it is coupled to the other vibrations. This observed phonon-vibronic coupling as well as the phonon-electronic coupling is consistent with the form of the force field proposed for the pyrazine crystal which consists of one term representing an intermolecular hydrogen bonding ($\text{C-H}\cdots\text{N}$) and two intermolecular hydrogen-hydrogen repulsion

terms. A change in the distribution of the hydrogen atoms (as produced by C-H vibrations) or the lone-pair electron density (as produced in $\pi^* \rightarrow n$ transition) can give rise to observed effects on lattice parameters and vice versa.

This work is described in detail in publication numbers 2, 3, and 4. Reports on these papers will follow this report.

II. Effects of Shallow Traps on Migration and Annihilation of Triplet Excitation in Molecular Crystals at Low Temperatures:

Delayed fluorescence originating from triplet-triplet annihilation is reported from a mixed crystal system characterized by an added impurity in low concentrations and large triplet trap depth. Temperature and impurity (guest) concentration dependence are extensively investigated in the anthracene in phenanthrene system. It is observed that for concentrations below 10^{-4} moles/mole, at temperatures below 50°K, host delayed fluorescence is independent of added anthracene and is best described as originating from triplet-triplet annihilation between host triplet and shallow triplet traps, whose phosphorescence emissions are found to correlate with the phenanthrene delayed fluorescence as the temperature is changed in the range 4.2° to 50°K. Near 77°K, these shallow traps become ineffective acceptors of host triplet excitation and delayed fluorescence arising mainly from the interaction between the anthracene and phenanthrene triplet excitations. The temperature dependence of the delayed fluorescence strongly supports the trapping and the de-trapping mechanism formulated by Siebrand. In this present system, two discernible shallow trap phosphorescences are observed. A kinetic model is proposed and supported by the observed dependence of the delayed fluorescence intensity on guest concentration,

temperature, exciting light intensity, as well as the observed activation energy.

This work is described in detail in a preprint sent for publication (publication number 9). The report concerning this work is now in preparation.

III. The Radiative and Nonradiative Properties of the Individual Multiplets of the Lowest Triplet State:

a. Spin Polarization and Spin-Lattice Relaxation in the Lowest Triplet State of Pyrazine at 1.6°K:

The different mechanisms proposed for the spin-lattice relaxation process of a paramagnetic impurity in ionic crystals are briefly summarized. The decay characteristics of the pyrazine phosphorescence in cyclohexane and benzene matrices at 1.6°K and its temperature dependence can best be explained if competition between the spin-lattice relaxation process between the triplet sublevels and the radiative process from one of the sublevels of pyrazine is invoked. Spin polarization in the $^3B_{3u}^{n,\pi^*}$ state of pyrazine at 1.6°K is achieved by the selection rules imposed on the intersystem crossing process, $^1B_{3u}^{n,\pi^*} \xrightarrow{\text{ISC}} ^3B_{1u}^{n,\pi^*} (\tau_y)$, followed by the fast internal conversion process $^3B_{1u}^{n,\pi^*} (\tau_y) \xrightarrow{\text{IC}} ^3B_{3u}^{n,\pi^*} (\tau_y)$. The latter sublevel (τ_y) of the $^3B_{1u}^{n,\pi^*}$ state is the emitting sublevel. This scheme is found to explain the observed temperature effects on the decay characteristics as well as the unique phosphorescence polarization along the N...N axis of the pyrazine molecule. Limits on the spin-lattice relaxation time (T_1), on the lifetime of the $T_1 \xrightarrow{\text{R}} S_0$ radiationless process and on the radiative lifetime of phosphorescence from the τ_x and τ_z sublevels of the $^3B_{3u}^{n,\pi^*}$ state of pyrazine at 1.6°K are determined. The effect of the magnetic field on the decay curve is demonstrated, and

briefly described.

b. The Intersystem Crossing to and Phosphorescence from the Individual Sublevels of the Lowest Triplet State in Pyrazine at 1.6°K:

The observed exponential phosphorescence decay of pyrazine in cyclohexane or benzene matrix at 77°K, with lifetime of 18 millisecc, is found to change into a complex decay below 10°K. At 1.6°K, the decay is resolved into three first-order decays of lifetimes 6, 130 and 400 millisecc. These lifetimes are sensitive to changes in temperature and magnetic field strength (Hall, Armstrong, Moomaw and El-Sayed, J. Chem. Phys., 48, 1395 (1968)). Two mechanisms are proposed to explain the observed results, but both propose that at 1.6°K, the spin-lattice relaxation process between the sublevels of the triplet state is slow compared to the 6-millisecc radiative lifetime of the τ_y spin sublevel. In the first mechanism, the 130- and 400-millisecc lifetimes measure the τ_x or $\tau_z \rightarrow \tau_y$ spin-lattice relaxation (S.L.R.) times, but the long- and medium-lived emissions originate from the τ_y sublevel. In the second mechanism, the 130- and 400-millisecc lifetimes correspond to radiative lifetimes of the transitions to the ground state from the τ_z and τ_x sublevels respectively. The recent time-resolved polarization measurements of pyrazine phosphorescence in durene (Moomaw, Tinti and El-Sayed, J. Chem. Phys., in press) indicate that the second mechanism should be at least partially responsible for the observed results.

The steady state intensity of the emission from the different sublevels of the ${}^3B_{3u}^{n,\pi*}$ state is determined from the decay curves. For molecules with

high phosphorescence yield, when the spin-lattice relaxation process is much slower than the radiative lifetimes, it can be shown that the ratio of the steady state intensity of the emission from the individual sublevels is equal to the ratio of the rate constants for the intersystem crossing processes to these sublevels. It is then concluded that the intersystem crossing process $^1B_{3u}^{n,\pi*} \rightsquigarrow ^3B_{1u}^{n,\pi*} \rightsquigarrow ^3B_{3u}^{n,\pi*}$ is ~ 30 times faster than other processes which require either vibronic interaction or strong enough crystal field to destroy the internal D_{2h} pyrazine symmetry.

The different radiative spin-orbit mechanisms which might give the different sublevels of the $^3B_{3u}^{n,\pi*}$ state their radiative properties are discussed and the relative values of the spin-orbit interaction energies involved are determined from the observed decay constants.

The above work is described in the publications numbered 5 and 6, and will be distributed soon.

IV. Review of Recent Studies on Triplet-Singlet Transitions in Aromatic Molecules:

A detailed review article has been written at the invitation of the Polish Academy of Sciences, in honor of the world-famous Polish spectroscopist, Dr. Jablonski. The paper is divided into four parts. The first part discusses the selection rules of the intersystem crossing process in systems having both n,π^* and π,π^* types of states. Using the Born-Oppenheimer approximation, first-order selection rules predict that the nonradiative singlet triplet transitions between states of different types (e.g., $S_{n,\pi^*} \rightarrow T_{\pi,\pi^*}$ or $S_{\pi,\pi^*} \rightarrow T_{n,\pi^*}$) should be two orders of magnitude more probable than those involving singlet and triplet states of the same electronic type (e.g., $S_{\pi,\pi^*} \rightarrow T_{\pi,\pi^*}$ and $S_{n,\pi^*} \rightarrow T_{n,\pi^*}$). This type of selection rule is known to result in a high degree of spin polarization

in the triplet states formed in these systems as well as in other systems in which one of the possible routes involved in the intersystem crossing process is favored over all the others (except when the molecule under examination belongs to the C_i or the cubic point groups). The detection of the polarized state by observing the phosphorescence emission requires that the radiative lifetime of the latter from at least one of the three sublevels of the lowest triplet state be shorter than the characteristic time for the spin-lattice relaxation processes between the three sublevels of the triplet state. This is demonstrated to be the case for pyrazine in its n, π^* triplet state at low temperatures (1.6° - 10°K) and discussed in Section III of the paper. The different mechanisms proposed for the spin-lattice relaxation process are briefly discussed. The observed spin-lattice relaxation times for pyrazine at 1.6° are found to be comparable to those observed for a number of ionic paramagnetic impurities in inorganic systems at the same temperature.

In the third part of the paper (Section IV), a summary of the theory of the triplet-singlet radiative transitions is given. A comparison of phosphorescence properties of the different systems is made and the observed differences are explained in the framework of the present theory. The phosphorescence of aromatic hydrocarbon is known to be the most forbidden electronic dipole transition known for polyatomic molecules. The reason for this is discussed in the paper, and the consequence of this fact is shown to be a great sensitivity of the triplet singlet radiative transition of these molecules to weak perturbations such as those produced by solvent effects and halogen substitution. Proposed explanations are given for the observed changes in the polarization of this transition resulting from these different weak perturbations.

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This review constitutes publication number 8. A copy of the review will be forthcoming with the technical report for this part of our activity.

PUBLICATIONS

of Work Supported by the Office of Naval Research

1. J. A. Duardo, F. M. Johnson and M. A. El-Sayed, "A New Method for Observing the Inverse Raman (Absorption) Spectra", Physics Letters, 21, 168 (1966).
2. W. R. Moomaw and M. A. El-Sayed, "Phosphorescence of Crystalline Pyrazine", J. Chem. Phys., 45, 3890 (1966).
3. W. R. Moomaw and M. A. El-Sayed, "Phosphorescence of Crystalline Pyrazine at 4.2°K", J. Chem. Phys., 48, 2502 (1968).
4. W. R. Moomaw and M. A. El-Sayed, "Phonon-Induced Phosphorescence in Pyrazine Molecular Crystal", J. Chem. Phys., 47, 2193 (1967).
5. L. Hall, A. Armstrong, W. Moomaw, and M. A. El-Sayed, "Spin-Lattice Relaxation and the Decay of Pyrazine Phosphorescence at Low Temperatures", J. Chem. Phys., 48, 1395 (1968).
6. M. A. El-Sayed, L. Hall, A. Armstrong, and W. R. Moomaw, "Spin Polarization and Spin-Lattice Relaxation in the Lowest Triplet State of Pyrazine at 1.6°K", in Excitons, Magnons and Phonons in Molecular Crystals, A. B. Zahlan, Editor; Cambridge University Press (1968).
7. M. A. El-Sayed, "The Intersystem Crossing to and the Phosphorescence from the Individual Sublevels of the Lowest Triplet State in Pyrazine at 1.6°K", in International Conference on Molecular Luminescence (Loyola University), E. Lim, Editor; W. Benjamin, Inc., in press.
8. M. A. El-Sayed, "Recent Studies on Triplet-Singlet Transitions in Aromatic Molecules", Acta Physica Polonica, in press.
9. E. M. Yee and M. A. El-Sayed, "Effects of Shallow Traps on Migration and Annihilation of Triplet Excitation in Molecular Crystals at Low Temperatures", J. Chem. Phys., in press.
10. M. A. El-Sayed and L. Hall, "Determination of the Rate Constants of the Intersystem Crossing Processes to the Individual Multiplets of the Lowest Triplet State", J. Chem. Phys., in press.

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